Sulfonated Microporous Organic-Inorganic Hybrids as Strong Bronsted Acids

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Approximately 50% of all industrial chemical processes require a catalyst. Catalysts lower the temperature and increase the rate of a reaction, making many difficult reactions commercially feasible. Sorbents are also greatly used in industry to recover the desired product from a chemical process or to separate and purify different compound types. We have developed a new class of materials that can function as sorbents and catalysts. The reaction of a zirconium compound with a disphosphonic acid of biphenyl , HO_3P PO_3H

in water yields layers of [Zr(O₃P)]_n that are cross-linked (linked together) by the biphenyl groups. However, if the reaction is carried out in organic (non-water) solvents, the products contain pores of molecular size (Figure 1). Molecules can be separated based upon size considerations and by preference of the molecules for the walls of the pore. By changing the nature of the pillars one can change the molecular preference to fit the type of separation required. The biphenyl groups can be sulfonated to convert the compound to a highly acidic catalyst. Many reactions may be carried out under mild reactions within the pores. These acid catalysts may replace highly corrosive, environmentally deleterious acids now in use. Our conception of how a layered cross-linked material may generate internal pores is depicted in Fig. 2.

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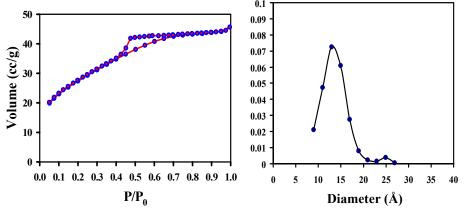


Figure 1. The N₂ adsorption-desorption isotherm and pore distribution

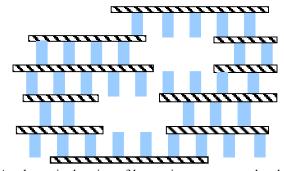


Figure 2. A schematic drawing of how micropores may develop in the zirconium biphenylenebis (phosphonates). The narrow rectangles shaded in blue represent the biphenyl pillars and the horizontal bars with parallel lines represent the ZrO₃P layers. The pillars bonded to only one layer and capped by a horizontal line at the other end represent unbonded phosphonic acid groups at the horizontal line. Such groups should also be present on the outer surfaces of the particle if an excess of Zr is not used in the synthesis.

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Education:

Recent work on this grant has produced two families of microporous materials with pores in the 10-20Å region. Many applications for these materials in separations science, ion exchange and catalysis are envisioned. To achieve these objectives we have put together a world wide team of collaborators that includes research groups in Spain, Poland and India. At right are pictured some of the team members: Zhike Wang – Graduate student Maria del Mar Gomez Alcantara – Visiting graduate student from University of Malaga, Spain Joy Heising – Post-doctoral Research Associate Student and Post-doctoral exchanges and visits with each of the groups are in the planning stages. Dr. Heising was voted the best teacher of chemistry 101-102 by the students in 2002-03. Six undergraduates are part of Prof. Clearfield's research group.

Outreach:

Professor Clearfield has explained superconductivity to two third grade classes and "Seeing Molecules and Atoms" to middle school students both with accompanying demonstrations.

